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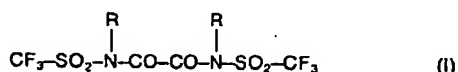
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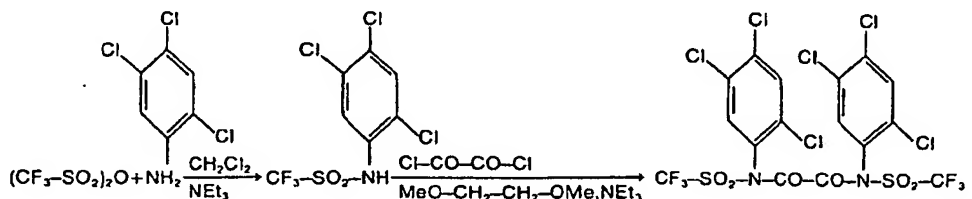
㉒ Novel N,N'-bis(trifluoromethylsulfonyl)oxamides, chemiluminescent compositions containing them and processes for generating chemiluminescence employing said compositions.

㉓ Novel N,N'-bis(trifluoromethylsulfonyl)oxamides of the formula (I)



wherein R and R' have the meaning given in the description (preferably chlorinated phenyl or pyridyl, nitrophenyl or methoxyethyl), when used in compositions comprising

also an organic fluorescer such as 1-chloro-9,10-bis(phenylethynyl)-anthracene and a diluent such as dibutyl phthalate, will furnish chemiluminescent light with good light intensity and quantum efficiency upon reaction with a peroxide component such as hydrogen peroxide. The preparation of the compounds of the formula (I) is described; e.g. the particularly preferred compound N,N'-bis(2,4,5-trichlorophenyl)-N,N'-bis-trifluoromethylsulfonyl-oxamide is prepared on the following way:



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TITLE: NOVEL N,N'-BIS(TRIFLUOROMETHYLSULFONYL)OXAMIDES,  
CHEMILUMINESCENT COMPOSITIONS CONTAINING THEM AND PROCESSES  
FOR GENERATING CHEMILUMINESCENCE EMPLOYING SAID COMPOSITIONS.

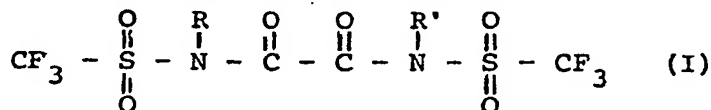
The present invention relates to novel N,N'-bis  
 (trifluoromethylsulfonyl)oxamide compounds, superior compo-  
 sitions containing said compounds which are useful for gen-  
 erating chemiluminescence by reaction with a hydroperoxide,  
 5 and a process for generating chemiluminescence by reacting  
 said superior compositions thereby.

The art has shown (Rauhut et al., U.S. Patent No.  
 3,442,815, and Maulding, U.S. Patent No. 3,400,080) that  
 oxamides when reacted under particular conditions provide  
 10 chemiluminescence. While the oxamides disclosed hitherto  
 provide substantially high light intensity, the efficiency  
 of the systems, as measured by the chemiluminescence quantum  
 yield, is one percent, or lower.

There is a need, therefore, for compositions that  
 15 will furnish superior light intensities over a long period  
 of time and have a chemiluminescence quantum efficiency  
 greater than one percent.

Summary of the Invention

In accordance with the present invention, there  
 20 are provided novel compounds represented by formula (I)



wherein R and R' independently represent hydrogen; alkyl of  
 25 1 to 6 carbon atoms; cycloalkyl of 4 to 8 carbon atoms; sub-  
 stituted alkyl or cycloalkyl wherein the substituents are

selected from halo, carboxy, alkoxy, or alkoxycarbonyl, wherein the alkoxy is of 1 to 6 carbon atoms; alkanoyl of 2 to 18 carbon atoms; aroyl of 7 to 11 carbon atoms; aralkyl of 7 to 11 carbon atoms; carbocyclic aryl of 6 to 10 carbon atoms; heterocyclic aryl of 3 to 9 carbon atoms; substituted carbocyclic and heterocyclic aryl of 6 to 10 and 3 to 9 carbon atoms, respectively, wherein the substituents, one or more, are selected from halo, nitro, cyano, trifluoromethyl, alkyl and alkoxy of 1 to 6 carbon atoms, hydroxy, phenoxy, benzyloxy, phenyl, alkanoylamino of 2 to 6 carbon atoms, benzoylamino, alkylsulfonyl of 1 to 6 carbon atoms, carboxy, alkoxycarbonyl and alkoxysulfonyl wherein the alkoxy group has 1 to 6 carbon atoms,  $-\text{SO}_3^{\ominus} \text{M}^{\oplus}$  wherein  $\text{M}^{\oplus}$  is a cation selected from sodium, potassium, lithium, ammonium, monoalkylammonium, dialkylammonium, trialkylammonium, or tetraalkylammonium wherein the alkyl radicals have 1 to 6 carbon atoms, and may be the same or different, aminocarbonyl, and amino-sulfonyl which are unsubstituted or substituted at the nitrogen by 1 or 2 radicals selected from alkyl of 1 to 6 carbon atoms, phenyl, or substituted phenyl, wherein the substituents are as defined above for carbocyclic and heterocyclic aryl.

In accordance with the present invention, there are also provided compositions for reaction with a peroxide component to generate chemiluminescence comprising (a) a compound of formula (I), as previously defined; (b) an organic fluorescer compound, and (c) a diluent, said ingredients being present in proportions and concentrations sufficient to produce chemiluminescence when reacted with said peroxide component.

In accordance with the present invention, there is also provided a process for generating chemiluminescence comprising reacting the composition described hereinabove with a peroxide component.

Chemiluminescence compositions of the novel compounds of formula (I) find a wide variety of applications in

emergency lighting devices (see U.S. Patent No. 3,800,132) for the home, on the road, in coal mines, on lifevests, and on aircraft escape slides.

The compounds of the present invention can be used to provide long lasting chemiluminescence. They are particularly distinguished from the oxamides of U.S. Patents Nos. 3,400,080 and 3,442,815 in that they provide superior chemiluminescence quantum yields, about 10-35%, versus about 1%, or lower, for the prior art oxamides.

10        Description of Preferred Embodiments

The Compounds of the present invention are readily prepared by reacting about two molecular proportions of the appropriate trifluoromethanesulfonamide, or trifluoromethanesulfonanilide, with oxalyl chloride in the presence of an acid-binding agent by methods well-known in the art.

Methods for the preparation of the trifluoromethanesulfonanilides and N-substituted trifluoromethanesulfonamides are known in the art (see Harrington et al., U.S. Patents 3,558,698; 3,629,332; 3,799,968; 3,865,844; 3,897,449; 20 3,920,444; and Moore et al., U.S. Patent 3,609,187).

Examples of the compounds of formula (I) include the following:

25        N,N'-diphenyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,

N,N'-dinaphthyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,

N,N'-bis(4-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

30        N,N'-bis(2-bromophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

N,N'-bis(4-fluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

35        N,N'-bis(3-iodophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

N,N'-bis(2,4-dichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

- N,N'-bis(2,4-dibromophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,5-difluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 5 N,N'-bis(4-bromo-2-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-chloro-4-fluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 10 N,N'-bis(2,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,4,6-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(3,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 15 N,N'-bis(2,4-dichloro-6-fluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,6-dichloro-4-fluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 20 N,N'-bis(2,3,5,6-tetrachlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,3,4,5,6-pentafluorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 25 N,N'-bis(2,4-dinitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-chloro-2-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 30 N,N'-bis(4-fluoro-3-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,5-dichloro-4-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,6-dichloro-4-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 35 N,N'-bis(4-cyanophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

- N,N'-bis(4-hydroxyphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-carboxyphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 5 N,N'-bis(4-ethoxycarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-ethoxysulfonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 10 N,N'-bis(4-aminocarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(3-aminosulfonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-chloro-5-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 15 N,N'-bis(2-nitro-4-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-bromo-2-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-fluoro-5-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 20 N,N'-bis(2,6-dinitro-4-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,6-dichloro-4-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 25 N,N'-bis[3,5-bis(trifluoromethyl)phenyl]-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(3-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-methylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 30 N,N'-bis(2,4-dimethylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-n-hexylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 35 N,N'-bis(4-chloro-2-methylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

- N,N'-bis(2-bromo-4-methylphenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-methyl-5-nitrophenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- 5 N,N'-bis(2-methoxyphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(4-n-hexyloxyphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2,5-dimethoxyphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 10 N,N'-bis(5-chloro-2-methoxyphenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(4-methoxy-2-nitrophenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- 15 N,N'-bis(5-chloro-2,4-dimethoxyphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(3-formylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-acetylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 20 N,N'-bis(3-n-hexanoylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(3-bromoacetylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 25 N,N'-bis(5-acetyl-2-methoxyphenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- N,N'-bis[2,4-bis(methylsulfonyl)phenyl]-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(4-acetamidophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 30 N,N'-bis(4-benzamidophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(3-propionamidophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 35 N,N'-bis(3-acetamido-4-chlorophenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,

- N,N'-bis(5-acetamido-2-methylphenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(3-acetamido-4-trifluoromethylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 5 N,N'-bis(2-acetamido-4-methoxyphenyl)-N,N'-bis-(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(5-chloroacetamido-2-methylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-chloro-5-chloroacetamidophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 10 N,N'-diethyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,
- N,N'-dihydro-N,N'-bis(trifluoromethylsulfonyl)-oxamide,
- 15 N,N'-di-n-butyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-di-n-propyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-dicyclohexyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 20 N,N'-dimethyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,
- N,N'-diisopropyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 25 N,N'-diacetyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,
- N,N'-dihexanoyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-diisobutyroyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 30 N,N'-bis(2-chloroethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-bromoethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 35 N,N'-bis(2-fluoroethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,



- N,N'-bis(trifluoromethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(3-chloropropyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 5 N,N'-bis(2-n-hexyloxyethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-nitroethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-dibenzyl-N,N'-bis(trifluoromethylsulfonyl)-oxamide,
- 10 N,N'-di-1-phenethyl-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-di-(1-naphthylmethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2,6-dichlorobenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 15 N,N'-bis(2-nitrobenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-cyanobenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 20 N,N'-bis(4-methylbenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(3-acetylbenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-methoxyethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 25 N,N'-bis(2-morpholyethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-piperidylethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 30 N,N'-bis(3-pyridyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-pyridyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 35 N,N'-bis(4-pyridyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

- N,N'-bis(2-chloro-3-pyridyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 5 N,N'-bis(2-furanyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-thienyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis[2-(2-pyridyl)ethyl]-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 10 N,N'-bis(2-thienyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(2-furfuryl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 15 N,N'-bis(4-methylsulfonylbenzyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(benzhydryl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-methylaminocarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 20 N,N'-bis(4-phenylaminocarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-o-bromophenylaminocarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 25 and the sodium, potassium, lithium, ammonium, methylammonium, n-hexylammonium, diethylammonium, tri-n-butylammonium, and tetraethylammonium salts of
- N,N'-bis(4-carboxyphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 30 N,N'-bis(2-carboxyphenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- N,N'-bis(4-sulfophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide, and
- N,N'-bis(2-sulfophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,
- 35 and the like.
- The preferred compounds are as follows:
- N,N'-bis(2,4-dichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

N,N'-bis(2,4,5-trichlorophenyl)-N,N'-bis-(trifluoromethylsulfonyl)oxamide,

N,N'-bis(2,4,6-trichlorophenyl)-N,N'-bis-(trifluoromethylsulfonyl)oxamide,

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N,N'-bis(4-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

N,N'-bis(2-methoxyethyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

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N,N'-bis(4-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

N,N'-bis(2-chloro-3-pyridyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide,

15 The particularly preferred compound is N,N'-bis-(2,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide.

The term "chemiluminescence", as employed herein, is defined as the generation of electromagnetic radiation between about 300 and 1200 nanometers by means of a chemical reaction.

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The term "composition for reaction with a peroxide component to generate chemiluminescence", as employed herein, is defined as a mixture of a compound of formula (I) and a fluorescer compound in a diluent in concentrations sufficient to produce chemiluminescence when combined with a peroxide component. Thus, the initial concentrations of the compound of formula (I), fluorescer compound, and the ingredients of the peroxide component in the reaction mixture must be sufficient to produce chemiluminescence.

25

30 The fluorescer compounds contemplated herein may be broadly defined as those which do not readily react with the peroxide component employed in this invention or with the compound of formula (I).

Typical fluorescent compounds for use in the present invention are those which have a spectral emission falling between 300 and 1200 nanometers and which are at least partially soluble in the diluent employed. Among these are the conjugated polycyclic aromatic compounds having at least

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3 fused rings, such as: anthracene, substituted anthracene, benzanthracene, phenanthrene, substituted phenanthrene, naphthacene, substituted naphthacene, pentacene, substituted pentacene, perylene, substituted perylene, violanthrone, substituted violanthrone, and the like. Typical substituents for all of these are phenyl, lower alkyl, chlorine, bromine, cyano, alkoxy ( $C_1 - C_{16}$ ), and other like substituents which do not interfere with the light-generating reaction contemplated herein.

10 Numerous other fluorescent compounds having the properties given hereinabove are well-known in the art. Many of these are fully described in "Fluorescence and Phosphorescence", by Peter Pringsheim, Interscience Publishers, Inc., New York, New York, 1969. Other fluoresters are described in "The Colour Index", Second Edition, Volume 2, The American Association of Textile Chemists and Colorists, 1956, pp. 2907-2923. While only typical fluorescent compounds are listed hereinabove, the person skilled in the art is fully aware of the fact that this invention is not so restricted, and that numerous other fluorescent compounds having similar properties are contemplated for use herein.

The preferred fluorester compound is a 9,10-bis-(phenylethynyl)anthracene, as disclosed in U.S. Patent 3,888,786, which is incorporated herein by reference.

25 The 9,10-bis(Phenylethynyl)anthracene compounds contemplated herein may be defined as 9,10-bis(phenylethynyl)-anthracene, or chloro, bromo, fluoro, or lower alkyl-substituted bis(phenylethynyl)anthracenes. The preferred compound is selected from 9,10-bis(phenylethynyl)anthracene or chloro-substituted 9,10-bis(phenylethynyl)anthracenes. More preferably, the compound is selected from 9,10-bis(phenylethynyl)anthracene, 1-chloro-9,10-bis(phenylethynyl)anthracene or 2-chloro-9,10-bis(phenylethynyl)anthracene.

35 Illustrative of the 9,10-bis(phenylethynyl)anthracenes which can be used in this invention are the following:

9,10-bis(phenylethynyl)anthracene,  
 1-chloro-9,10-bis(phenylethynyl)anthracene,  
 2-chloro-9,10-bis(phenylethynyl)anthracene,  
 5 1,5-dichloro-9,10-bis(phenylethynyl)anthracene,  
 1,8-dichloro-9,10-bis(phenylethynyl)anthracene,  
 1-bromo-9,10-bis(phenylethynyl)anthracene,  
 1-fluoro-9,10-bis(phenylethynyl)anthracene,  
 10 1-methyl-9,10-bis(phenylethynyl)anthracene,  
 and the like.

The term "diluent", as used herein, is defined as a solvent, or vehicle, which does not cause insolubility of the compound of formula (I), or any of the ingredients of  
 15 the peroxide component, and in which the fluorescer compound is at least partially soluble.

The term "peroxide component", as used herein, means a solution of a hydrogen peroxide compound, a hydroperoxide compound, or a peroxide compound in a suitable diluent.  
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The term "hydrogen peroxide" includes (1) hydrogen peroxide and (2) hydrogen peroxide-producing compounds.

The composition for reaction with a peroxide component to generate chemiluminescence can contain any fluid  
 25 diluent which solubilizes the compound of formula (I) and the fluorescer compound to provide initial concentrations in the reacting system of about  $10^{-3}$  M to about 10M, preferably about  $10^{-2}$  M to about 1 M, of the compound of formula (I), and about  $10^{-5}$  M to about  $10^{-1}$  M, preferably about  $10^{-4}$  M to  $10^{-2}$  M,  
 30 of the fluorescer compound. The diluent must be relatively unreactive toward the compound of formula (I), the fluorescer compound, and the ingredients of the peroxide component.

The concentrations of the compound of formula (I) and the fluorescer compound in the composition for reaction  
 35 with the peroxide component is about 1.1-2.-5, preferably about 1.2-1.3, times the concentrations of the same materials in the reacting system described above. Typical diluents,

or solvents, which can be used include esters, ethers, aromatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons such as those disclosed in U.S. Patent No. 3,749,679. The preferred diluent is dibutyl phthalate. Solvent combinations may, of course, be used but such combinations should not include strongly electron donating solvents.

Hydrogen peroxide is the preferred hydroperoxide and may be employed as a solution of hydrogen peroxide in a solvent or as an anhydrous hydrogen peroxide compound such as sodium perborate, sodium peroxide, and the like. Whenever hydrogen peroxide is contemplated to be employed, any suitable compound may be substituted which will produce hydrogen peroxide.

Diluents which can be employed in the peroxide component include any fluid which is relatively unreactive toward the hydroperoxide, the compound of formula (I) and the fluorescer compound, and which accommodates a solubility to provide at least 0.01M hydroperoxide. Typical solvents for the hydroperoxide component include water; alcohols, such as ethanol, tertiary butanol, or octanol; ethers, such as diethyl ether, diamly ether, tetrahydrofuran, dioxane, dibutyldiethyleneglycol, perfluoropropyl ether, and 1,2-di-methoxyethane; and esters, such as ethyl acetate, ethyl benzoate, dimethyl phthalate, dioctylphthalate, propyl formate. Solvent combinations can, of course, be used such as combinations of the above with anisole, tetralin, and chlorobenzene, providing said solvent combination accommodates hydroperoxide solubility. However, strong electron donor solvents such as dimethyl formamide, dimethyl sulfoxide, and hexamethylphosphoramide should not, in general, be used as a major diluent for the peroxide component.

The preferred diluent for the peroxide component is a mixture of about 80 volume percent dimethyl phthalate and about 20 volume percent tertiary butanol.

The hydrogen peroxide concentration in the peroxide component may range from about 0.2M to about 15M. Preferably, the concentration ranges from about 1M to about 2M.

The lifetime and intensity of the chemiluminescent light emitted can be regulated by the use of certain regulators such as:

(1) By the addition of a catalyst which changes  
5 the rate of reaction of hydroperoxide with the compound of formula (I). Catalysts which accomplish that objective include those described in M. L. Bender, "Chem. Revs.", Vol. 60, p. 53 (1960). Also, catalysts which alter the rate of reaction or the rate of chemiluminescence include those  
10 accelerators of U.S. Patent No. 3,775,366, and decelerators of U.S. Patent Nos. 3,691,085 and 3,704,231, or

(2) By the variation of hydroperoxide. Both the type and the concentration of hydroperoxide are critical for the purposes of regulation.

15 Preferably, a weakly basic accelerator, such as sodium salicylate, is included in the peroxide component to control the lifetime of the chemical lighting system. The concentration of weakly basic accelerator used in the peroxide component may range from about  $10^{-6}$  M to about  $10^{-2}$  M, preferably from about  $10^{-4}$  M to about  $10^{-3}$  M.  
20

The initial concentration of the ingredients of the peroxide component in the reacting system is about 0.15 to 0.60 of the concentrations in the peroxide component since the peroxide component comprises about 15 to about 60 volume  
25 percent of the reaction mixture.

The concentration of the hydrogen peroxide compound in the chemiluminescent reaction is at least equal to the molar concentration of the compound of formula (I) and is preferably 1.2 to 5.0 times the concentration of the compound  
30 of formula (I) in the reacting system described above. The optimum concentrations must be determined experimentally for each specific system.

The following examples are illustrative of the present invention. All parts are by weight unless otherwise indicated.  
35

EXAMPLE 1Preparation of N-2,4,5-Trichlorophenyl-Trifluoromethanesul-  
fonamide

Trifluoromethanesulfonic anhydride (14.11 grams;  
5 0.05 mole) is added in portions to a stirred solution of 2,4,  
5-trichloroaniline (9.8 grams; 0.05 mole) and triethylemine  
(5.0 grams; 0.05 mole) in methylene chloride (50 mls) at 0°C  
under a nitrogen atmosphere. The reaction mixture is stir-  
red at 0°C for one hour upon completion of the addition, then  
10 heated to 50°C and stirred thereat for 3 hours. The white  
solid precipitate is separated by filtration and the filtrate  
is evaporated to obtain a dark oil. Water (40 mls) is added  
to the oil and the resulting mixture is extracted three times  
with diethyl ether (50 mls). The combined ethereal extracts  
15 are then dried over anhydrous sodium sulfate, the dried ex-  
tract is separated and the separated ethereal solution is  
evaporated to obtain 13.4 grams of crude product. Recry-  
stallization of the crude product from methylcyclohexane  
gives the desired product, m.p. 104-106°C.

20 Analysis - Calculated for  $C_7H_3Cl_3F_3NO_2S$  (percent):  
C, 25.69; H, 0.92; Cl, 32.11; F, 17.43; N, 4.28; S, 9.  
79

Found (percent):  
C, 25.59; H, 1.00; Cl, 31.98; F, 17.00; N, 4.28; S,  
25 9.95

In the manner described above and in U.S. Patent  
No. 3,799,968, using the appropriately substituted anilines,  
and amines, the following compounds are prepared:

30 N-phenyltrifluoromethanesulfonamide,  
N-(4-chlorophenyl)trifluoromethanesulfonamide,  
N-(2,4-dichlorophenyl)trifluoromethanesulfonamide,  
N-(2,4,5-trichlorophenyl)trifluoromethanesulfonamide,  
35 N-(2,4,6-trichlorophenyl)trifluoromethanesulfonamide,  
N-(4-nitrophenyl)trifluoromethanesulfonamide,



N-(2-methoxyethyl)trifluoromethanesulfonamide,  
N-methyltrifluoromethanesulfonamide,  
N-(2-bromoethyl)trifluoromethanesulfonamide,  
5 N-(2-chloro-3-pyridyl)trifluoromethanesulfonamide,  
N-(2-chloroethyl)trifluoromethanesulfonamide,  
N-(2-morpholyethyl)trifluoromethanesulfonamide,  
and N-(2-piperidylethyl)trifluoromethanesulfonamide.

10

EXAMPLE 2Preparation of N,N'-Bis(2,4-dichlorophenyl)-N,N'-Bis(Tri-fluoromethylsulfonyl)Oxamide

Oxalyl chloride (1.90 grams; 0.015 mole) is added dropwise to a solution of N-2,4-dichlorophenyltrifluoromethanesulfonamide (5.94 grams; 0.02 mole) and triethylemine  
15 (2.0 grams; 0.02 mole) in 1,2-dimethoxyethane (50 mls) at 0°C under a nitrogen atmosphere. After the addition is completed, the reaction mixture is heated to 70°C and held thereat for 5 hours. The reaction mixture is filtered to  
20 remove insolubles and the filtrate is evaporated to obtain 6.05 grams (94% of theoretical) of crude product.

Recrystallization of the crude product from cyclohexane affords the desired product, m.p. 148-150°C.

25 Calculated for  $C_{16}H_6N_2O_6Cl_4F_6S_2$ : C, 29.95%; H, 0.90%; N, 4.36%; Cl, 22.12%; F, 17.75%; S, 10.00%  
Found: C, 30.24%; H, 1.02%; N, 4.24%; Cl, 22.27%; F, 17.19%; S, 10.45%

EXAMPLE 3

30 Preparation of N,N'-Bis(2,4,5-trichlorophenyl)-N,N'-Bis(tri-fluoromethylsulfonyl)oxamide

Method A:

Oxalyl chloride (1.27 grams; 0.01 mole) is added portionwise to a stirred solution of N-2,4,5-trichlorophenyl trifluoromethanesulfonamide (6.2 grams; 0.02 mole) and triethylamine (2.0 grams; 0.02 mole) in methylene chloride (50  
35 mls) at 0°C under a nitrogen atmosphere. After the addition is completed, the reaction mixture is stirred at room temp-

erature for about 4 hours and then filtered to obtain 2.1 grams of crude product.

Recrystallization of the crude product from methylcyclohexane affords the desired product, m.p. 190-192°C.

5           Calculated for  $C_{16}H_4N_2O_6Cl_6F_6S_2$ : C, 27.02%; H, 0.57%;  
N, 3.94%; Cl, 29.91%; F, 16.04%; S, 9.02%  
Found: C, 27.02%; H, 0.63%; N, 3.84%; Cl, 30.06%;  
F, 16.64%; S, 8.90%

10           Evaporation of the filtrate, obtained by isolating  
the crude product and triturating the residue with water,  
gives an additional 3.5 grams of crude product after filtering and drying. The total yield in two crops is 78.7% of theoretical.

Method B:

15           Oxalyl chloride (4.44 grams; 0.035 mole) is added  
in portions to a suspension of N-2,4,5-trichlorophenyl trifluoromethylsulfonamide (15.0 grams; 0.06 mole) and powdered molecular sieves (15 grams; Molecular Sieve, Type 3A from Union Carbide Corporation) in methylene chloride (150 mls) at  
20   0°C under a nitrogen atmosphere. After the addition is completed, the reaction mixture is heated to 60°C and stirred thereat for 5 hours. The molecular sieves are then separated by filtration and the filtrate is concentrated to remove the methylene chloride and obtain 17.45 grams (82%  
25   of theoretical) of crude product.

Recrystallization of the crude product from methylcyclohexane gives a product identical with that obtained by Method A.

EXAMPLE 4

30   Preparation of N,N'-Bis(4-nitrophenyl)-N,N'-Bis(trifluoromethylsulfonyl) Oxamide

Oxalyl chloride (0.825 gram; 0.0065 mole) is added dropwise to a stirred solution of N-4-nitrophenyl trifluoromethanesulfonamide (3.61 grams; 0.013 mole) and triethylamine (1.3 grams; 0.0128 mole) in dry tetrahydrofuran (40 mls) at 0°C under a nitrogen atmosphere. After the addition is completed, the reaction mixture is warmed

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to room temperature and stirred thereat for 18 hours. The reaction mixture is then filtered, the solvent is evaporated from the filtrate, and water (20 mls) is added to the residue. The resulting precipitate is then filtered to obtain 3.29 grams (92% of theoretical) of crude yellow-colored product.

Recrystallization of the crude product from diethyl ether gives the desired product, m.p. 172-175°C.

Calculated for  $C_{16}H_8N_4O_{10}F_6S_2$ : C, 34.16%; H, 1.42%;

10 N, 9.96%; F, 20.28%; S, 11.39%

Found: C, 34.46%; H, 1.25%; N, 9.80%; F, 19.82%;

S, 11.78%

#### EXAMPLE 5

#### Preparation of N,N'-Bis(2-methoxyethyl)-N,N'-Bis(trifluoromethylsulfonyl)Oxamide

Oxalyl chloride (1.27 grams; 0.01 mole) is added portionwise to a stirred solution of N-(2-methoxyethyl) trifluoromethanesulfonamide (4.0 grams; 0.02 mole) and triethylamine (2.0 grams; 0.02 mole) in 1,2-dimethoxyethane (40 mls) at 0°C under a nitrogen atmosphere. After the addition is completed, the reaction mixture is stirred at 0°C for one hour, heated to 50°C and stirred thereat for 2 hours, and concentrated to remove the solvent. The residue is then extracted with diethyl ether and the ether extract is evaporated to obtain 4.65 grams (99% of theoretical) of crude product.

Vacuum distillation of the crude product gives the pure product, b.p. 74-76°C at 0.5 mm.

Calculated for  $C_{10}H_{14}N_2O_8F_6S_2$ : C, 25.64%; H, 2.99%;

30 N, 5.98%; F, 24.36%; S, 13.68%

Found: C, 25.60%; H, 3.11%; N, 5.77%; F, 23.95%;

S, 13.92%

#### EXAMPLE 6

#### Preparation of N,N'-Bis(4-chlorophenyl)-N,N'-Bis(trifluoromethylsulfonyl)Oxamide

Oxalyl chloride (0.635 gram; 0.005 mole) is added dropwise to a stirred solution of N-4-chlorophenyl-trifluoro-

- 19 -

methanesulfonamide (2.6 grams; 0.01 mole) and triethylamine (1.0 gram; 0.01 mole) in 1,2-dimethoxyethane (20 mls) at 0°C under a nitrogen atmosphere. The mixture is stirred at 0°C for 2 hours, heated to 60°C and held at 60°C for one hour, and evaporated to obtain a yellow solid which is then treated with 20 mls of water.

Recrystallization of the remaining solid from anhydrous ether gave 2.46 grams of the desired product as white crystals which melted at 173-174°C. The yield is 85.8% of theoretical.

Calculated for  $C_{16}H_8N_2Cl_2S_2O_6F_6$ : C, 33.50%; H, 1.40%; N, 4.88%; Cl, 12.40%; S, 11.17%; F, 19.90%

Found: C, 33.51%; H, 1.38%; N, 4.74%; Cl, 12.10%; S, 11.52%; F, 19.11%

15

EXAMPLE 7Preparation of N,N'-Bis(2-chloro-3-pyridyl)-N,N'-Bis(trifluoromethylsulfonyl)Oxamide

Oxalyl chloride (0.762 gram; 0.006 mole) is added dropwise to a suspension of N-(2-chloro-3-pyridyl)trifluoromethanesulfonamide (2.61 grams; 0.01 mole) and powdered molecular sieves (5.0 grams; Molecular Sieve, Type 3A) in methylene chloride (75 mls) at 0°C under a nitrogen atmosphere. The mixture is then heated to 60°C, held thereat for 3 hours, and then stirred at room temperature for 60 hours. The reaction mixture is filtered and the filtrate is evaporated to dryness. The resulting residue is extracted with diethyl ether, and the combined ethereal extracts are dried over anhydrous sodium sulfate. The dried ethereal extract is then separated and evaporated to obtain 2.33 grams (81% of theoretical) of crude product.

Recrystallization of the crude product from cyclohexane gives the desired product, m.p. 104-106°C.

Calculated for  $C_{14}H_6N_4O_6Cl_2F_6S_2$ : C, 29.27%; H, 1.05%; N, 9.76%; Cl, 12.20%; F, 19.86%; S, 11.15%

35

Found: C, 29.10%; H, 1.14%; N, 9.51%; Cl, 11.95%; F, 19.40%; S, 10.89%

In the manner described above using 0.01 mole of

the appropriately substituted trifluoromethanesulfonamide, the following compounds are prepared:

- N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 5 N,N'-bis(di-n-butyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-dihexanoyl-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-bromoethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 10 N,N'-bis(2-chloroethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-n-hexyloxy)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 15 N,N'-bis(dibenzyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2,6-dichlorobenzyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis[2-(2-pyridyl)ethyl]-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 20 N,N'-bis(2-furfanyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-thienyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- 25 N,N'-bis(4-aminocarbonylphenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide,
- N,N'-bis(2-morpholyethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide, and
- N,N'-bis(2-piperidylethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

30

#### EXAMPLE 8

##### Determination of Chemiluminescence

A solution (7.5 mls) of 1-chloro-9,10-bis(phenylethynyl)anthracene (CBPEA) and the reactant under study, in dibutyl phthalate, is mixed with 2.5 mls of peroxide

35 component comprising hydrogen peroxide and sodium salicylate in 80% dimethyl phthalate - 20% tertiary butanol, by volume to provide a reaction mixture having initial concentrations

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of 0.38M hydrogen peroxide,  $0.3 \times 10^{-3}$ M sodium salicylate,  
6.75  $\times 10^{-3}$ M CBPEA, and the concentration of reactant in-  
dicated in Table I, and quantitative measurements of the  
chemiluminescence of the different systems are carried  
5 out by measuring the intensity of the light emitted at 555  
nanometers by means of a Hirt-Roberts radiometer-spectro-  
photometer. The results obtained are summarized in Table I.

10

15

20

25

30

35

TABLE I

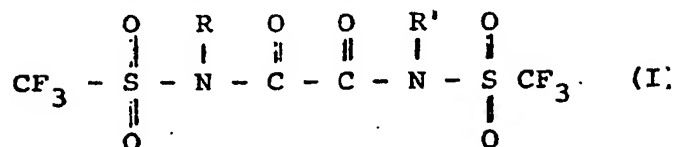
<u>Reactant</u>	<u>Conc.</u> <u>(Molar)</u>	<u>a</u>		<u>b</u>	
		<u>Light Capacity</u>		<u>Quantum Yield</u>	
Compound of Example 3	0.01	112.50		34.00	
" "	0.01	37.47		11.44	
" "	0.01	35.70		11.00	
" "	0.1	69.89		21.40	
" "	0.1	9.20		2.85	
" "	0.008	41.30		15.50	

a. Lumen hours per liter of emitting solution

b. Einsteins per mole x 10<sup>2</sup>

CLAIMS:

1. A compound represented by formula (I)



wherein R and R' independently represent hydrogen; alkyl of 1 to 6 carbon atoms; cycloalkyl of 4 to 8 carbon atoms; substituted alkyl or cycloalkyl wherein the substituents are selected from halo, carboxy, alkoxy, or alkoxycarbonyl, wherein the alkoxy is of 1 to 6 carbon atoms; alkanoyl of 2 to 18 carbon atoms; aroyl of 7 to 11 carbon atoms; aralkyl of 7 to 11 carbon atoms; carbocyclic aryl of 6 to 10 carbon atoms; heterocyclic aryl of 3 to 9 carbon atoms; substituted carbocyclic and heterocyclic aryl of 6 to 10 and 3 to 9 carbon atoms, respectively, wherein the substituents, one or more, are selected from halo, nitro, cyano, trifluoromethyl, alkyl and alkoxy of 1 to 6 carbon atoms, hydroxy, phenoxy, benzyloxy, phenyl, alkanoylamino of 2 to 6 carbon atoms, benzyloxy, phenyl, alkanoylamino of 2 to 6 carbon atoms, benzoylamino, alkylsulfonyl of 1 to 6 carbon atoms, carboxy, alkoxycarbonyl and alkoxysulfonyl wherein the alkoxy group has 1 to 6 carbon atoms,  $-\text{SO}_3^{\ominus} \text{M}^{\oplus}$  wherein  $\text{M}^{\oplus}$  is a cation selected from sodium, potassium, lithium, ammonium, monoalkylammonium, dialkylammonium, trialkylammonium, or tetraalkylammonium wherein the alkyl radicals have 1 to 6 carbon atoms, and may be the same or different, aminocarbonyl, and aminosulfonyl which are unsubstituted or substituted at the nitrogen by 1 or 2 radicals selected from alkyl of 1 to 6 carbon atoms, phenyl, or substituted phenyl wherein the substituents are as defined above for carbocyclic and heterocyclic aryl.

2. The compound according to Claim 1: N,N'-bis (4-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

3. The compound according to Claim 1: N,N'-bis (2,4-dichlorophenyl)-N,N'-bis (trifluoromethylsulfonyl) oxamide.



4. The compound according to Claim 1: N,N'-bis (2,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

5. The compound according to Claim 1: N,N'-bis (2,4,6-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

6. The compound according to Claim 1: N,N'-bis (4-nitrophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

7. The compound according to Claim 1: N,N'-bis (2-methoxyethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

8. The compound according to Claim 1: N,N'-bis (2-chloro-3-pyridyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

9. The compound according to Claim 1: N,N'-bis (2-chloroethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide.

10. A composition for reaction with a peroxide component to generate chemiluminescence comprising (a) a compound as defined in any of the preceding claims, (b) an organic fluorescer compound, and (c) a diluent, said ingredients being present in proportions and concentrations sufficient to produce chemiluminescence when reacted with said peroxide component.

11. A process for generating chemiluminescence, characterized by reacting a peroxide component with a composition as defined in Claim 10.

12. A process according to Claim 11, wherein said peroxide component is hydrogen peroxide.

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European Patent  
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# EUROPEAN SEARCH REPORT

0010844  
Application number

EP 79301845.8

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.) 3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	US - A - 3 855 261 (PYONG-NAE-SON) + Claim 1 + --	1	C 07 C 143/74 C 09 K 11/07 C 09 K 11/06
	FR - A - 2 093 605 (BAYER) + Examples 3, 16, 20; claim 1 + --	1	C 09 K 11/00 C 09 B 67/00
	US - A - 3 637 845 (GEORGE G.I. MOORE) + Claim 1 + --	1	
	DE - B - 1 293 741 (BAYER) + Column 1 + --	1	TECHNICAL FIELDS SEARCHED (Int. Cl.) 3
	DE - A1 - 1 792 774 (AMERICAN CYANAMID) + Claim 1 + --	1, 10-12	C 07 C 143/00 C 07 C 145/00 C 09 K 11/00 C 09 B 67/00
	GB - A - 1 163 436 (AMERICAN CYAN.) + Page 18, No.4; claim 1 + ----	1, 10-12	
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			8: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search VIENNA		Date of completion of the search 11-01-1980	Examiner REIF

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